



# Internal pressure measurements of the binary 0.7393H<sub>2</sub>O + 0.2607NH<sub>3</sub> mixture near the critical and maxcondetherm points

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## ABSTRACT

The pressure,  $P$ , and their temperature derivative  $(\partial P/\partial T)_V$ , of binary mixture 0.7393H<sub>2</sub>O + 0.2607NH<sub>3</sub> has been measured in the near- and supercritical regions. Measurements were made in the immediate vicinity of the liquid–gas coexistence curve (one- and two-phase regions) using a high-temperature, high-pressure, nearly constant-volume adiabatic piezo-calorimeter. Measurements were made along 40 liquid and vapor isochores in the range from 120.03 kg m<sup>-3</sup> to 671.23 kg m<sup>-3</sup> and at temperatures from 403 K to 633 K and at pressures up to 28 MPa. Temperatures at the liquid–gas phase transition curve,  $T_S(\rho)$ , for each measured density (isochore) were obtained using the quasi-static thermograms technique. The expanded uncertainty of the pressure,  $P$ , and temperature derivative,  $(\partial P/\partial T)_V$ , measurements at the 95% confidence level with a coverage factor of  $k=2$  is estimated to be 0.05% and 0.12–1.5% (depending on temperature and pressure), respectively. The direct measured pressures,  $P$ , and temperature derivatives,  $(\partial P/\partial T)_V$ , has been used to calculate the internal pressure (or energy–volume coefficient) as  $(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P$ . We also measured the temperature derivatives of the internal energy  $(\partial U/\partial T)_V = C_V$  (isochoric heat capacity) using the same apparatus. The measurements were made at isochoric heating of the system at quasi-equilibrium conditions. The effect of pressure, temperature, and concentration on the internal pressure was studied. The measured values of pressure ( $P_S$ ), temperature derivative,  $(\partial P/\partial T)_{V_S}$ , temperature ( $T_S$ ) and density ( $\rho_S$ ) at the saturation curve together with isochoric heat capacity measurements were used to calculate other thermodynamic properties of the mixture at the bubble- and dew-pressure points curves. Some unusual “appendix type shape” behavior of the  $(\partial P/\partial T)_V$  and internal pressure,  $P_{\text{int}}$ , near the critical and maxcondetherm points (in the retrograde region) was found.

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## 1. Introduction

In this work we directly measured pressures,  $P$ , and their temperature derivatives,  $(\partial P/\partial T)_V$ , of the binary mixture 0.7393H<sub>2</sub>O + 0.2607NH<sub>3</sub> in the immediate vicinity of the liquid–gas phase transition curve near the critical and maxcondetherm points. The measured pressures,  $P$ , and temperature derivatives,  $(\partial P/\partial T)_V$ , has been used to calculate the internal pressure (energy–volume coefficient) as

$$P_{\text{int}} = \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P, \quad (1)$$

or equivalent form

$$P_{\text{int}} = \left( \frac{\partial U}{\partial V} \right)_T = T \frac{\alpha_P}{K_T} - P, \quad (2)$$

where  $T$  is the temperature,  $V$  is the specific volume,  $P$  is the pressure,  $U$  is the internal energy,  $P_{\text{int}}$  is the internal pressure,  $K_T$  is the isothermal compressibility, and  $\alpha_P$  is the isobaric coefficient of thermal expansion. Using the same apparatus, we also measured the temperature derivatives of the internal energy (energy–temperature coefficient),  $(\partial U/\partial T)_V = C_V$ , isochoric heat capacity. Internal pressure of liquids is very useful tool in understanding the molecular interactions, internal structure, and ordered structure of binary mixtures. Internal pressure is the result of the forces of attraction and repulsion between molecules in a liquid. The accurate direct measurements of the internal pressure of fluids and fluid mixtures are known to give valuable information regarding the nature of the intermolecular interactions. Therefore, internal pressure is very important to understand of the nature of molecular interactions and in the theory of liquid and liquid mixtures. Internal energy–volume coefficient,  $(\partial U/\partial V)_T$ , is very

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sensitive to changes in the structure of the binary mixtures, nature of the interaction between solute and solvent molecules. The statistical mechanical definition of the internal energy and internal pressure is

$$U = \frac{3}{2}NkT + \frac{1}{2}N \int_0^{\infty} g(r)\phi(r)dr, \quad (3)$$

$$P_{\text{int}} = -\frac{2\pi}{3}\rho^2kT \int_0^{\infty} r^3 \frac{\partial\phi}{\partial r} \frac{\partial g}{\partial r} dr, \quad (4)$$

where  $\phi(r)$  is the potential energy between a pair molecules separated by a distance  $r$  and  $g(r)$  is the radial distribution function (probability of finding a molecule at a distance  $r$  from the reference molecule). The relation (4) can be used to modeling of the intermolecular interaction and structural properties of fluids and fluid mixtures on the bases of measured internal pressure data by using the molecular simulation techniques (MC and MD). It is obviously that for ideal gas the internal pressure is zero (no interaction between the molecules), while for real gases and liquids it significantly deviate from zero and much greater than the pressure. Intermolecular forces create a pressure within a liquid of between  $10^2$  and  $10^3$  MPa. A high internal pressure implies strong intermolecular cohesion. When liquid isothermally changing the volume does work against the cohesive forces which are causes changes in the internal energy.

The internal pressure,  $(\partial U/\partial V)_T = P_{\text{int}}$ , and isochoric heat capacity,  $(\partial U/\partial T)_V = C_V$ , i.e. volume and temperature derivatives of the internal energy, describes the sensitivity of internal energy  $U$  to a change in specific volume  $V$  and temperature  $T$  at the isothermal and isochoric processes, respectively. Therefore, direct simultaneous measurements of  $P_{\text{int}}(T, V)$  and  $C_V(T, V)$  provides the caloric equation of state  $U(V, T)$  which is significantly accurate than thermal  $P(V, T)$  equation of state (EOS).

Most cases the derivative  $(\partial P/\partial T)_V$  (thermal-pressure coefficient) calculated from the EOS like Tait type, cubic, or multiparametric EOS. The direct measurements of the derivative  $(\partial P/\partial T)_V$  are very rare. Indirect method of determination of the internal pressure based on the measurements of  $K_T$  and  $\alpha_P$  (see above Eq. (2)). Usually, the values of these  $K_T$  and  $\alpha_P$  derived from speed of sound and PVT measurements. Dack [1] determined the internal pressure of several solutions at 25 °C with a constant volume apparatus. The uncertainty in internal pressure determination in this method is about 2%. Dack [1] and Barton [2] are performed direct measurements of derivative  $(\partial P/\partial T)_V$  from experimental determined heat of vaporization as  $P_{\text{int}} = (\Delta H_{\text{vap}} - RT)/(M/\rho)$ , where  $M$  is the molecular weight,  $\rho$  is the density, and  $\Delta H_{\text{vap}}$  is the enthalpy of vaporization. This is most frequently used method. Shukla et al. [3] studied the internal-pressure coefficient and its correlation with solubility and pseudo-Gruneisen parameters for binary and multicomponent liquid mixtures over a wide range of concentration at 298 K using the measured values of viscosity, density, and ultrasonic velocity. Grant-Taylor and Macdonald [4] determined thermal-pressure coefficient of acetonitrile + water mixture at temperatures between 298 K and 328 K using 25 ml glass constant volume cell. The measured  $P$ - $T$  isochores were fitted with the linear equation  $P = (\partial P/\partial T)_V T + C$ . The derived values of  $(\partial P/\partial T)_V$  were corrected for the finite expansion and compression of glass. The measured values of  $(\partial P/\partial T)_V$  were used to derive the energy-volume  $(\partial U/\partial V)_T$  (internal pressure) coefficient and other thermodynamic quantities. The uncertainty of the derived values of  $(\partial P/\partial T)_V$  is 2%. Macdonald and Hyne [5] reported thermal-pressure and energy-volume coefficients measurements for dimethyl sulfoxide + water mixtures at temperatures between 13 °C and 55 °C and at atmospheric pressure by using the same technique. Some

authors [6,7] derived the values of internal-pressure coefficient from the direct measurements of the isothermal compressibility  $K_T$  and isobaric coefficient of thermal expansion  $\alpha_P$  by using the Eq. (2). Zorębski [6] studied the effect of pressure on the internal pressure. Goharshadi and Nazari [8] also studied temperature and pressure effect on the internal pressure of liquids using the statistical mechanical EOS. Kumar et al. [9] used measured ultrasonic velocity and density data to study internal pressure of binary mixtures (acetone- $\text{CCl}_4$  and acetone-benzene). The measured data were used to study of the molecular interactions in binary liquid mixtures. Vadamarai et al. [10] also used acoustic and viscometric parameters to accurate calculate the internal pressure for binary mixtures of tert-butanol and isobutanol with methyl methacrylate. Verdier and Anderson [11] used indirect method to estimate the values of internal pressure of mixtures, using thermal expansivity (determined by microcalorimeter) and isothermal compressibility (determined by density measurements). Korolev [12] studied internal pressure of alcohols using the values of volumetric coefficient (thermal expansion and isothermal compressibility coefficients). Westwater et al. [13] and Smith and Hildebrand [14] directly measured  $(\partial P/\partial T)_V$  using the constant-volume thermometer apparatus. The liquid is confined to a glass bulb with a capillary neck in which its level may be maintained at a fixed point by an electrical contact to a mercury interface. The coefficient  $(\partial P/\partial T)_V$  is found directly as the slope of a graph of pressure against temperature for liquid in such apparatus. The isochoric  $P$ - $T$  curves are almost straight line, except at the critical point, where the temperature dependence of the pressure  $P(\rho_C, T)$  along the critical isochore is  $\propto (T - T_C)^{2-\alpha}$ . Therefore, their slopes are easily to accurate measure in the range far from the critical point. The thermal-pressure coefficient  $(\partial P/\partial T)_V$  changes smoothly without any anomaly with temperature, even at the critical point, although the second temperature derivative discontinuity (weakly diverges) at the critical point as  $(\partial^2 P/\partial T^2)_V \propto (T - T_C)^{-\alpha}$ , where  $\alpha = 0.11$  universal critical exponent of the isochoric heat capacity. The acoustic method was used by Dzida [15] to calculate the internal pressure of cyclopentanol at pressures up to 100 MPa and at temperatures from 293 K to 318 K. McLure and Arriaga-Colina [16] reported thermal-pressure coefficient measurements for ethanenitrile, propanenitrile, and butanenitrile from 297 K to 398 K. Measurements were made with an apparatus consisting of a constant-volume thermometer in which the pressure is controlled and measured for a series of temperatures at a series of different constant densities. McLure et al. [17] also measured of the thermal-pressure coefficient for five dimethylsiloxane oligomers in the temperature range from 298 K to 413 K. Thermal-pressure coefficients were measured in Pyrex cells (dilatometers). The sample was confined by mercury, and changes in its volume were monitored by weighing the amount of mercury expelled from or drawn into the dilatometer. Measured isochore slopes,  $(\partial P/\partial T)_V$ , were corrected using the effect of the thermal expansion and compression of both quartz and mercury. The uncertainty in thermal-pressure coefficient measurements is about 1.0%. Suryanarayan [32] derived the expression for the internal pressure on the basis of dimensional analysis using free volume concept.

Temperature dependency of the internal pressure (temperature coefficient) can be estimated from the Eq. (1) as

$$\left(\frac{\partial P_{\text{int}}}{\partial T}\right)_V = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V, \quad (5)$$

or,

$$\left(\frac{\partial P_{\text{int}}}{\partial T}\right)_V = \left(\frac{\partial C_V}{\partial V}\right)_T. \quad (6)$$

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